Synthesis, Characterization and Ion-Exchanging Properties of a Novel Ion-Exchange Resin, Part II

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A polyamine (PA) was prepared by condensation of 1,4-bischloromethyl benzene and 1,2-thanediamine. This PA was then treated with cyanuric chloride at 0°C followed by reaction with 5-amino-8-hydroxyquinoline in THF in conc. NaOH (PH 9-10) at room temperature for 8 h. The resultant polymer, designated as polyamine-s-triazine-5-amino-8-hydroxyquinoline (PATHQ), was characterized by elemental analysis, IR spectral studies, and thermogravimetry. The PATHQ was monitored for its chelating and ion-exchanging properties. The polymeric metal chelates of PATHQ with Cu^{2+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, UO_2^{2+} and Co^{2+} metal ions were prepared and characterized by metal:ligand ratio, IR and reflectance studies, magnetic properties, thermogravimetry and microbicidal activity. The batch equilibration method has been adopted for evaluation of ion-exchange properties.

INTRODUCTION

The effluents from mines and metal industries set up serious problems in removal of heavy toxic metal ions. The contents of these metals in effluent are almost above the legal limit [1–3]. The content of these metals can be reduced by treatment with lime, but the results are not satisfactory. Thus the ion-exchange technique has proved very useful in this context. The ion-exchange resins can be used for metal extraction from ore, analytical reagent, and the separation of metal

ions and deionization of water [4–9]. Most commercial ion-exchange resins are sulfonated polystyrene-divinylbenzene copolymers [10–11]. The use of complex ion-formation in ion-exchange resin has been considered to solve the problem [10–11]. The aim of the present work's to prepare and study a novel ion-exchange resin. Thus one the authors [AS] reported recently a novel ion-exchange resin [12]. In continuation of this work [12], the present paper comprises the synthesis of novel ion-exchange resin containing a well-known metal complexing agent and 8-hydroxyquinoline and its chelating and ion-exchanging properties. The synthetic route is shown in Scheme 1 below:
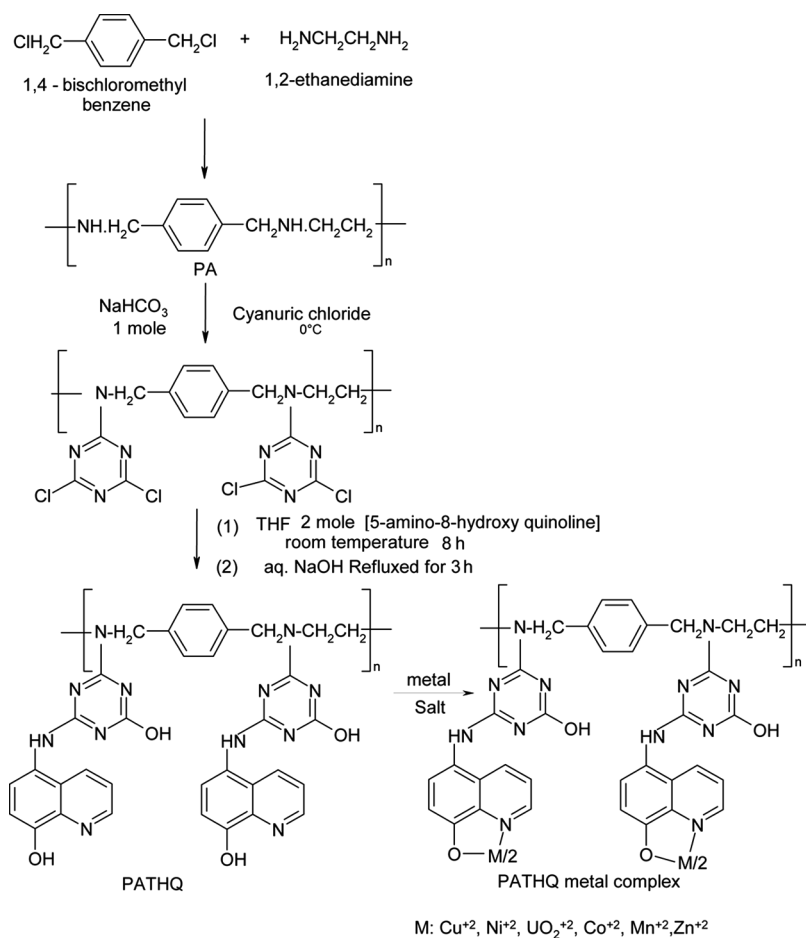
SCHEME 1 Synthetic procedure.

EXPERIMENTAL

MATERIALS

All the chemicals used were of either pure or analytical grade.

The synthesis of polyamine (PA) and PA-triazine (PAT) resin was prepared by a method reported in an earlier communication [12]. 5–amino–hydroxy quinoline was prepared by a method reported in the literature [13].

Synthesis of PAT-5-Amino-8-Hydroxyquinoline (PATHQ)

To a mixture of PAT polymer (0.01 mole) and 5-amino-8-hydroxyquinoline (0.02 mole) in THF (100 ml), conc. NaOH was added while maintaining pH 9–10 of the mixture. The mixture was heated to 60°C gently for 5 min and was the stirred at room temperature for 8 h. The resulting gel type material was filtered, washed by water and air-dried. It was powdered to 100 mesh size. Yield was 90%. It did not melt up to 300°C and was insoluble in water and common organic solvents.

Synthesis of Polymeric Chelates

The polymeric metal chelates of PATHQ were synthesized by reaction of PATHQ with corresponding metal acetates. The detailed procedure is as follows.

A dried PATHQ polymer (0.01 mole) was dispersed in 200 ml solution of 20% aqueous formic acid and warmed on a water bath for 10 min. To this dispersed solution a warm solution of metal acetate (0.01 mole) in 50% aqueous formic acid was added dropwise with constant stirring. The reaction mixture was made alkaline with dilute ammonia in order to coagulate polymeric chelates. The resultant products were further digested in a water bath for an hour. Finally the solid polymer chelates were filtered off washed with hot water followed by acetone and DMF, and dried in air. Copolymer chelates of PATHQ with Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, UO_2^{2+} and Zn^{2+} transition metal ions were prepared.

MEASUREMENTS

Elemental analyses for C, H and N content were carried out on a TF 1101 elemental analyzer (Italy). IR spectra of polymer ligand and their metal chelates were scanned on a NICOLET 760 DR FTIR spectrophotometer in KBr phase. The metal content of polychelates were

determined by decomposing a weighed amount of each polymer chelate followed by EDTA titration as reported in literature [14].

Magnetic susceptibility measurements of all the polychelates were carried out at room temperature by the Gouy method using mercury tetrathiocyanato cobaltate (II), Hg [Co (NCS)$_4$], as a calibrant. The diffuse reflectance spectra of all the solid polychelates were recorded on a Backman DK-2A spectrophotometer with solid reflectance attachments. MgO was employed as the reference compound. Thermal behavior of these metal chelates were studied by TGA, perfomed on a thermogravimetric analyzer.

The batch equilibration method was adopted for the ion-exchanging properties [15,16]. The evaluation of the influence of different electrolytes on metal uptake by the polymer, the rate of metal uptake under specified conditions and distribution of various metal ions of different pH values were carried out following the details of the procedures described earlier[15,16].

RESULTS AND DISCUSSION

The polymer sample PATHQ was in the form of dark brown powder, insoluble in common organic solvents. It swells up to some extent in conc. NaOH solution. It did not melt up to 300°C. The elemental contents in Table 1 are consistent with the predicted structure. The number of –OH groups per unit of PATHQ were found to be four. The IR spectrum comprises the bands due to secondly NH (3400 cm^{-1}), methylated group (2930, 2850, 1430 cm^{-1}), s-triazine and aromatic 8HQ moieties (3030, 1500, 1600 cm^{-1}). The TGA of PATHQ contains single-step degradation. The degradation starts from 280°C, rapid loss between 300 to 500 and lost almost 85% at 650°C.

Characterization of Polymeric Chelates

The polymeric chelates of PATHQ with the metal ions of Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+} UO$_2^{2+}$ and Zn^{2+} vary in color from dark green to brown. They generally resemble each other. Comparison of IR spectra of the parent ligand with then polymer chelates has revealed certain differences as mentioned below.

One of the significant differences to be expected between IR spectrum of parent ligand and its metal chelates is the absence of a broad band in the region of 3370–3450 cm^{-1} due to O-H stretching vibration frequencies in IR spectrum of polymer chelates as, the oxygen of this O-H of parent ligand has formed a bond with the metal ion.

TABLE 1 Analyses of Polymeric Metal Chelates of PATHQ and their Metal Chelates

Sample designation	Elemental analysis				μeff	Thermal analysis					
	N %		M %		B.M	% Weight loss at different temperature °C					
	Cald	Found	Cald	Found		200	300	400	500	600	700
PATHQ	25.14	24.78	—	—	—						
PATHQ (Cu^{2+})	20.26	19.87	15.31	14.92	1.78	0.9	1.5	15	51	67	83
PATHQ (Ni^{2+})	20.51	20.09	14.28	13.87	3.00	1.1	8	23	55	70	92
PATHQ (UO_2^{2-})	13.52	13.12	43.47	43.12	D	2	11	28	57	75	91
PATHQ (CO^{2+})	20.48.	20.01	14.39	14.14	4.03	1.7	10	23	63	70	94
PATHQ (Mn^{2+})	20.68	20.22	13.54	13.21	4.68	1.8	12	24	62	75	95
PATHQ (Zn^{2+})	20	19.13	16.42	16.04	D	1	8	17	56	65	92

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Another noticeable difference is that the 8-quinolinol band at 1606 cm^{-1} in IR spectrum of PATHQ is assigned to implane O-H deformation and this is shifted towards higher frequency in the spectra of polymer chelates, indicating the formation of metal-oxygen bonds [17–19]. This has been further confirmed by a weak band at 1100 cm^{-1} corresponding to C-O-M stretching frequency [17–19]. All these characteristic features of IR suggest the general structure of polymer chelates as shown in Scheme I.

Examination of data about metal content in each polymer chelate (Tables 1 and 2) has revealed a 1:1 metal:ligand stoichiometry in all the polychelates. Magnetic moment (μ_{eff}) data of polymer chelates given in Table I have revealed that all metal chelates like Cu^{2+}, Ni^{2+} and Co^{2+} are paramagnetic, while that of Zn^{2+} is diamagnetic in nature. The electronic spectra of PATHQ with Cu^{+2} ions show two broad bands at 14950 and 23529 cm^{-1} due to $^2T1_g \rightarrow ^2E_g$ transition and charge transfer, respectively, suggesting a distorted octahedral structure for PATHQ polymer chelates. The PEAQ with Ni^{2+} and Co^{+2} ion polychelates each gives two absorption bands respectively at 14925, 24096 cm^{-1} and 14925, 22471 cm^{-1} corresponding to $^4T_g \rightarrow ^2T_{1g}$, $^4T_{1g} \rightarrow ^4T_{1g}(P)$ transition [20–22]. Thus, absorption bands of diffuse reflectance spectra and the values of magnetic moment (μ_{eff}) have indicated an octahedral configuration for the Ni^{2+}, and Co^{2+} polychelates. The spectra of polychelates of Mn^{2+} ion show two weak bands at 17241 cm^{-1} and 25031 cm^{-1} assigned to the transition $^6A_{1g} \rightarrow ^4T_{2g}$ (4 G) and $^6T_{1g} \rightarrow ^4T_{1g}(4 G)$, respectively, and assigned an octahedral structure for PATHQ chelates. As the spectrum of the Zn^{2+} chelates is not well-resolved it is not interpreted, but its μeff value reveals its diamagnetic nature as expected. The TGA data (TG thermograms not shown) of all polymeric chelates are shown in Table 1. The TGA data reveal that the rate of decomposition of all polymeric chelates is initially low, up to 200°C temperature, and rapidly increases to maximum in the range 400–500°C. This might be due to accelerated in situ catalyzed formation of metal oxide of all these polychelates.

Ion-Exchange Properties

The examination of data presented in Table 2 reveals that the amount of metal ions taken up by a given amount of the PATHQ polymer depends upon the nature and concentration of the electrolyte present in the solution. The amounts of Fe^{3+}, Cu^{2+} and UO_2^{2+} ions taken up by the polymer sample increase with the increase in concentration of ions like chloride, chlorate and nitrate but decrease with the increase in

TABLE 2 Influence of Different Electrolytes on the Uptake of Several Metal Ions ($[Mt (NO_3)_2] = 0.1$ mole$\cdot$l^{-1})[a]

Metal ions	pH	[Electrolyte] (mole$\cdot$l^{-1})	Adsorption of mmol. 10^1 of the metal ion on PATHQ polymer[b]			
			NaClO$_4$	NaNO$_3$	NaCl	Na$_2$SO$_4$
Cu^{2+}	5.5	0.01	0.08	0.06	0.13	0.27
		0.05	0.17	0.08	0.14	0.26
		0.1	0.13	0.14	0.16	0.25
		0.5	0.26	0.16	0.19	0.23
		1.0	0.42	0.20	0.24	0.19
Fe^{3+}	2.75	0.01	0.09	0.11	0.01	0.19
		0.05	0.20	0.14	0.02	0.05
		0.1	0.23	0.15	0.06	0.07
		1.0	0.32	0.24	0.23	0.05
UO$_2^{2+}$	4.0	0.01	0.17	0.15	0.13	0.22
		0.05	0.21	0.16	0.15	0.23
		0.1	0.15	0.24	0.19	0.25
		0.5	0.24	0.45	0.21	0.19
		1.0	0.54	0.45	0.24	0.16
Co^{2+}	5.5	0.01	0.13	0.14	0.09	0.05
		0.05	0.12	0.13	0.11	0.06
		0.1	0.05	0.14	0.08	0.05
		0.5	0.03	0.06	0.06	0.04
		1.0	0.01	0.02	0.03	0.01
Mn^{2+}	5.5	0.01	0.21	0.24	0.21	0.16
		0.05	0.18	0.21	0.18	0.11
		0.1	0.15	0.19	0.21	0.07
		0.5	0.12	0.17	0.20	0.03
		1.0	0.10	0.19	0.15	0.01
Zn^{2+}	5.5	0.01	0.12	0.06	0.09	0.12
		0.05	0.11	0.06	0.09	0.02
		0.1	0.09	0.07	0.04	0.06
		0.5	0.03	0.05	0.01	0.02
		1.0	0.02	0.02	0.01	0.01
Ni^{2+}	5.5	0.01	0.07	0.12	0.01	0.18
		0.1	0.21	0.14	0.02	0.04
		0.5	0.22	0.14	0.06	0.06
		1.0	0.33	0.22	0.22	0.04

[a]Volume of electrolyte solution 40 ml, time 24 h, volume of metal ion solution 1 ml, temp. 25°C.
[b]Wt of PATS polymer 25 mg.

concentration of sulfate ions. The amounts of the remaining three metal ions Co^{2+}, Mn^{2+}, and Zn^{2+}, taken by the polymer sample decrease with the increase in concentration of chlorate, chloride, nitrate and sulfate ions.

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TABLE 3 Comparison of the Rates of Metal (Mt) Ion Uptake[a]

Time (h)	Attainment of equilibrium state[b], %			
	Fe^{3+}	UO_2^{2+}	Cu^{2+}	Mn^{2+}
0.5	63.2	32.1	35.9	22.8
1	72.3	67.2	52.3	47.3
2	89.5	85.6	64.2	63.7
3	92.1	92.2	75.3	77.1
4	91.2	96.9	84.6	84.8
5	—	—	90.2	86.6
6	—	—	94.8	92.6
7	—	—	94.3	98.3

[a][Mt $(NO_3)_2$] = 0.1 mole·l^{-1}, volume 1 ml, [$NaNO_3$] = 1 mol·l^{-1}, volume 40 ml pH = 3, temp 25°C, wt of PATS polymer 25 mg.
[b]Related to the amount of metal ions taken up at the state of equilibrium assumed to be established in 24 h and assumed to be 100%.

Rate of Metal Uptake

The rates of metal absorption by the PATHQ sample were measured for Fe^{3+}, UO_2^{2+}, Cu^{2+} and Mn^{2+} ions in the presence of 1 M $NaHCO_3$ to know the time required to reach the stage of equilibrium. All experiments were carried out at pH 3. A examination of the results presented in Table 3 shows that UO_2^{2+} and Fe^{3+} ions required slightly more than 3 h for the establishment of equilibrium and Cu^{2+} and Mn^{2+} ions required about 5 h for the purpose. In the experiments with solution containing UO_2^{2+} and Fe^{3+} ions, more than 70% of equilibrium was established in the first hour. This reveals that the rate of uptake of metal ions follows the order UO_2^{2+}, $Fe^{3+} > Cu^{2+} > Mn^{2+}$. The rates of uptake of Zn^{2+} and Co^{2+} ions have been found to be very low at pH 3. Hence the values are not reported.

DISTRIBUTION RATIO OF METAL IONS AT DIFFERENT pH VALUES

The results described in Table 4 reveal that the amount of metal ions taken up by the polymer sample PATHQ at equilibrium increases with the increase in pH. The selectivity of the polymer sample UO_2^{2+} and Fe^{3+} ions are higher than that for each of the remaining metal ions. The distribution ratio for Fe^{3+} ions is lower than that for UO_2^{2+} by about 1800 units at pH 3. The lower values of the distribution ratio for Fe^{3+} ions requires its attachment with proper sites on three different polymer chains and that of the UO_2^{2+} ion requires such an

TABLE 4 Distribution Ratios, D, of Different Metal Ions as a Function of the pH

	Distribution ratio[a] of metal ions[b]					
pH	Cu^{2+}	Fe^{3+}	UO_2^{2+}	Co^{2+}	Mn^{2+}	Zn^{2+}
1.5	—	—	249	—	—	—
1.75	124	126	425	—	—	—
2.0	160	165	514	—	—	—
2.5	445	448	544	—	—	—
3.0	944	945	2787	—	—	—
4.0	—	—	—	3	74	77
5.0	—	—	—	77	136	136
6.0	—	—	—	335	257	256

[a]mmol of metal ions taken up by 1 g of polymer mmol of ions present in 1 ml of solution $[Mt(NO_3)_2] = 0.1 \, mol \, l^{-1}$, volume: 1 ml; wt. of polymer: 25 mg; $[NaNO_3] = 1 \, mol \, l^{-1}$, volume: 44 ml; temp.: 25°C, time 24 h (equilibrium state).

[b]Error +/−5%.

attachment with sites on two polymer chains. Among the remaining metal ions, Cu^{2+} has a high value of distribution ratio at pH 6 while the other three metal ions Co^{2+}, Zn^{2+}, and Mn^{2+} have a low distribution ratio over a pH range from 4 to 6. Further work in the direction of the wide range of such polymers and their ion-exchanging properties is under progress.

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